Atmospheric Chemistry and Physics Discussions

Interactive Comment

Interactive comment on "The relative importance of competing pathways for the formation of high-molecular-weight peroxides in the ozonolysis of organic aerosol particles" *by* M. Mochida et al.

M. Mochida et al.

We thank the referees for providing valuable feedbacks and acknowledging the importance of this work. Here we address our responses to the referees' comments.

***** Reply to the comments by Referee #1 *****

1) p. 7152, l. 2: When discussing the fate of SOZ1, there is discussion that SOZ1 was not observed in the particles, but could be present below "our detection limit". I did not find any information on what the detection limit is for the different product types or how that detection limit was evaluated. Was a detection limit of the AMS determined in the analysis of these product types? If so, provide details as to what that limit is and how it was determined.

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Reply: The discussion was not accurate. The intensity of the peak of SOZ1 at m/z 267 is small, but it is above the detection limit. In the revised manuscript, the small abundance of SOZ1 relative to SOZ2 and SOZ3 is explained based on the low I^{267}/I^{311} ratio (0.07). (Sect. 3.3, last para.)

2) Section 3.6, Assessment of the relative importance of competing reactions. It would be helpful for the authors to add more commentary on the comparison of experimental modeling results. For example, as a result of this comparison, the authors state that k2:k1 can be contained between 0.3 and 3 for mixing ratios less than 0.5. This spans a wide range of values where k2 can be less, equally, and more important to product formation than k1. I would like to see the authors add more interpretation as to the overall significance of this comparison.

Reply: Taking into account the simplification of the model (e.g., formation of diperoxides is not included) and the magnitude of measurement errors, we think that the tone of the explanation in Sect. 3.6 is reasonable.

3) Consistency should be maintained between figures and text when referencing ion fragments in the text. In some locations, ion fragments are labeled M-X, while in other locations (and figures), they are labeled [M-X]+. Ion fragments should be consistently labeled in the text as [M-X]+. Specific locations where this needs to be corrected are listed below. Technical corrections needed: 1) nm s1 needs to be changed to nm s-1 at the following locations: p. 7144, l. 20; p. 7148, l. 13; p. 7148, l. 22. 2) change ion fragment references to [M-X]+ p. 7149, l. 20-26 p. 7150, l. 1-9 p. 7151, l. 28 3) p. 7154, l. 9: "t

Reply: They are corrected.

***** Reply to comments by Referee #2 *****

Both reviewers highlight the impact of high molecular weight (HMW) products for CCN activity. An equally important impact is gas particle partitioning: The primary products

in Fig. 2 (NN, OAME, NA, AAME) are volatile or semivolatile. If HMW products did not form, most of the aerosol mass would be lost upon reaction. The possibility of a significant loss of aerosol mass owing to oxidation has been suggested in the literature (Molina, Ivanov, Trakhtenberg, Molina, Geophysical Research letters (2004) 31(22), Art. No. L22104). Mochida et al. show that aerosol mass loss for the MO system is relatively small. It would be very interesting to study how the competition between primary product evaporation and HMW product formation changes as the particle size decreases. An increasing surface to volume ratio should favor evaporation. The authors performed this experiment with relatively large particles (500 nm dia.) which favors volume processes such as HMW formation over surface processes such as evaporation. Can the experiment be repeated, for example, with 100 nm dia. particles to probe this effect?

Reply: We agree that the volatilization of organics in particles by oxidation is a very important issue, although the investigation on the particle yield as a function of initial particle diameter is beyond the focus of this study. A brief explanation for the importance of this kind of study was added to the conclusion section.

It is well known from the authors' previous work and from the work of others (e.g. Baer) that the kinetics of oleic acid ozonolysis is complex. However, the discussion in section 3.1 avoids this topic. Since the main motivation for using MO over oleic acid is the potential for a simplified product distribution, it is important to understand how the kinetics mechanisms compare as well. For example, is there evidence for surface shell polymerization during MO ozonolysis as is observed with oleic acid? How well do the data in Fig. 3 fit an exponential vs. square root time dependence? Please comment on the mechanism in some detail.

Reply: The detailed kinetics mechanism of the ozonolysis of organic particles is beyond the scope of this study, and extensive additional experiments and analyses would be necessary to assess the kinetics mechanisms. Fitting of the O_3 decay by quadratic or exponential time dependence may not clarify the diffusive length of O_3 in particles

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because the characteristics of particles (e.g., solubility of O_3) change as the ozonolysis products accumulate in particles.

Finally, the reproducibility (repeat measurements at a given time) and repeatability (repeat measurements on different days/weeks) should be addressed. Is the product distribution (relative signal intensities) stable over time? Or is there an inherent instability associated with the cascade of reactions leading to the formation of specific HMW products?

Reply: Reproducibility is given by error bars in the figures. We have added an sentence explaining the repeatability of peak intensities in the last paragraph in Sect. 3.1.

***** Reply to the comments by Referee #3 *****

(Comment 6 is incomplete and a reply to it is not included.)

2) Page 7138, lines 23-25: the last sentence is misleading, giving the impression that these are the first results to suggest that HMW organic peroxides could result from ozonolysis of unsaturated organic molecules in the atmosphere. This has already been shown by several groups previously, as acknowledged by the authors. The focus of this report is on a quantitative measure of these organic peroxides. I would suggest that this last sentence be removed.

Reply: The sentence in the abstract was changed to: "The results therefore suggest that SCI's in atmospheric particles contribute to the transformation of carboxylic acids and other protic groups into HMW organic peroxides."

4) Page 7143, line 4: Was the interaction time of 6 s determined experimentally, or estimated from simple flow considerations? This should be clarified.

Reply: The interaction time was calculated based on the consideration that particles are transferred at the center of the Poiseuille flow in the flow tube reactor. The residence time of particles in a connection tube between the flow tube and the AMS is negligibly small. We have added this explanation to Sect. 2.2, 1st paragraph.

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5) Page 7143, line 24: Again, the interaction time of "0 s" with the injector tube fully inserted is a "reference zero" for this particular study. Was this measured experimentally or is it simply the shortest interaction time that serves as the "0 point?"

Reply: The 0 s residence time was experimentally established by placing the inlet and outlet face to face by inserting the injector tube. See Sect. 2.3, 1st paragraph.

7) Page 7146, lines 22-24: The authors discuss bis(acyloxy-1-alkyl) peroxides (BAAP's , see lines 233-237) and reference older works by Rebrovic and Nishikawa. Ziemann [1] has a much more recent observation and discussion of these types of peroxides and should be referenced and possibly this work should be discussed. Moreover, Ziemann's observation is based on the ozonolysis of aerosols, as compared to the works of Rebrovic and Nishikawa. These latter reports were for solution-based bulk chemistry and might be considered less relevant that Ziemann's work.

Reply: The Ziemann's work for oleic acid ozonolysis is explained in the revised text. See Sect. 3, 2nd paragraph.

8) Page 7147, line 20: The value of the uptake coefficient has an associated error, but no error bars are evident in Figure 3.

Reply: Error bars have been added to the figure.

9) Page 7147, line 20: Is the reference to Katrib et al 2005 a) or b) or both?

Reply: Katrib et al., 2005b is correct.

10) Page 7148, line 13: How was the evaporation rate of reacted particles determined? Since the particles were "reacted to completion," what served as the zero evaporation time? This should be clearly detailed.

Reply: We changed the residence time of reacted particles (27 or 45 s) in the system by using short or long piece of tubing. This is explained in the revised manuscript. (See Sect. 3.2, 1st para. and the caption of Table 1.)

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11) Page 7148, line 24: What is the justification for inference that the sum of the volume fractions of the four LMW products has an upper limit of 5

Reply: As explained in the next sentence, this inference is based on the assumption that the rate of evaporation is nearly proportional to the mole fraction (and thereby volume) of the volatile products. This is clarified in the revised text. (Sect. 3.2, 1st para.)

12) Page 7149: This entire discussion should be clarified extensively. Try as I might, I was not able to reproduce the numbers with the data provided in Table 1. In fact, the authors appear to have used data that is not reported in the Table. For example, the authors calculate a ratio of particle masses before and after ozone exposure, but in order to calculate this ratio, the mobility diameter of the reacted particles is needed; however, only the aerodynamic diameters (as determined with the Aerodyne instrument) are given in the Table.

Reply: The explanation in Sect 3.2 has been revised. The d_m value at 6 s is approximated by that at 27 s, on the assumption that the rate of evaporation of MO ozonolysis products between 6 to 27 s is very low, as observed between 27 and 45 s.

13) Page 7149, lines 10-11: The authors state that a correction could be applied for evaporative losses of the products but that they did not apply the correction. Why not?

Reply: The explanation was not accurate and the sentence has been changed to: "MO volatilization is negligible because of complete reaction within 2 s based upon the reaction kinetics." (Sect. 3.2, 2nd para.)

14) Page 7149, lines 14-15: The authors are making a second inference based on a first, unsubstantiated inference (see item "i.")

Reply: The first inference is explained more clearly. (See our reply to the comment 11.) We think that this second inference is worth presenting in the paper.

16) Page 7166, Table 1: The caption is not clear, especially regarding the longer res-

idence times of 27 and 45 seconds. Do the authors physically change the tubing between the flow tube and the DMA? If so, what tubing length was used for the "0" and "6" s measures? I assume that there was always some connecting tubing present. Are the "2" and "20" seconds in addition to the tubing used typically? Assuming that there was always some tubing connecting the flow tube to the DMA, then "0" and "6" second residence times were actually longer. How much? This should all be clarified.

Reply: We used different pieces of tubing for 2 s and 20 s residence times between the flow tube and the DMA (which correspond to 27 and 45 residence times in total, respectively). This explanation has been added to the caption of Table 1. The 0 and 6 s residence times are not for the SMPS measurement, but for the AMS measurement. The residence time between the flow tube and the AMS is negligibly short (0.25 s), as explained in the revised text. (Sect. 2.2, 1st para.)

17) Figure 2: The products observed should be indicated with underlining. For example, the authors observe SOZ2/3 but not SOZ1, which they discuss in the text, yet are not clear on the figure.

Reply: The absence of the product peaks is in some cases caused by evaporation (e.g., LMW products and SOZ1). The presence/absence of product peaks thereby does not necessarily corresponds to the formation pathways. To avoid misreading, we leave Figure 2 as it was.

19) The authors focus on secondary chemistry that forms peroxide particles but a mechanism for oxygenation by ketone formation has been proposed for OL [2], observed for the ozonolysis of OL[3, 4], and in unsaturated methyl esters[5]. This route should be discussed. If it is an unimportant route in these MO based systems that should noted and justified.

Reply: The formation of ketones, according to the fresh evidence in the two recent Zahardis papers, is included in the discussion in the revised manuscript. In the particular work reported in this manuscript, however, the expected fragment peaks for ketones

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(methyl oxo-stearate) were absent, suggesting that the ketones were at most minor products, at least for the reaction conditions employed. (Sect. 3.5)

20) Kinetic analysis: In general, more details are needed on the reactive uptake calculations: Is the calculation of the uptake coefficient data driven or model driven? If the calculation is (resistor) model driven, what is the limiting case regime used? This regime should be discussed in context of not only other findings for MO, but OL as well since there are still questions about the reactive uptake of ozone by the OL system being a surface reaction or limited by the diffusion of ozone within the particle - did the reactive uptake of measurements using MO provide additional insight about the reactive uptake by OL, which has been adopted as a model heterogeneous reaction system?

Reply: The kinetic analysis is based on a initial decay rate of MO. The gamma was calculated on the assumption that mole of MO reacted is equal to that of ozone. This is explained in the revised text. The detailed kinetics mechanism (e.g., surface or bulk-diffusion reaction) is beyond the focus of this study and thus it is not discussed in the text.

1) Page 7138, line 9: Reference to specific companies should not be made in the Abstract, unless central to the science, which is not the case here. The specific reference to "Aerodyne" should be removed. 3) Page 7142, line 6: The term "atomizing" in the second line of Sec. 2.1 is a misnomer (although commonly used). There is no atom formation taking place. The correct terminology is "nebulizing." 15) Page 7166, Table 1: First line should read "increasing reaction time" 18) Figure 3: Error bars should be included. If smaller than the data symbols (which I don't think is the case), it should be stated.

Reply: They are corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7137, 2006.

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